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NOTES IN REGARD TO THE DETERMINATION OF COPPER IN WATER.

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IN the course of a series of experiments carried on by the Massachusetts State Board of Health it became necessary to devise a method for separating and determining quantitatively small amounts of copper in water; such a method has been worked out and is published in detail in the "Standard Methods of Water Analysis" of the Laboratory Section of this Association.[1] It is the purpose of this short paper to give a brief outline of the method, together with some experimental results, and to call attention to certain statements that have appeared in print regarding the total disappearance of the copper in a few hours when applied to a water supply, and the impossibility of detecting it in the water by chemical tests.

The chemical test in general use for detecting copper in solution in small quantities is that mentioned by Moore and Kellerman in *Bulletin 64* of the Bureau of Plant Industry, and consists of adding potassium ferrocyanide to the solution to be tested, acidified by acetic acid. The sensitiveness of this test is shown by the following figures.

.00001 gm. copper, as copper sulphate, in 20 c.c. distilled water, equivalent to 1 part copper in 2,000,000, gave a very faint color, which it would be impossible to identify as the characteristic red of the reaction. 0.00002 gm. copper in 20 c.c. water, equivalent to 1 part copper in 1,000,000, gave distinctly the characteristic color. Both these strengths of copper solution were tested also in volumes of 100 c.c. in tubes, in order to observe the colors through a longer column than in the previous experiments, but with the same results.

The above tests were made with a solution of copper sulphate in distilled water, no other substances being present. It is well known that the presence of iron seriously interferes with the test, and it has been found that the coloring matter of natural waters is also a troublesome factor, so that in practice the sensitiveness of the test is much less than is indicated by the figures obtained with solutions in distilled water. A considerable quantity of water can be concentrated to small volume in order to increase the value of this test, but it then becomes necessary to provide for the removal of iron and organic coloring matter, or the results obtained are of doubtful significance.

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[1] *Jour. Infect. Dis.*, 1905, Supplm. No. 1, p. 1.

Among various published accounts of the treatment of water supplies with copper sulphate, the writers have noticed in several cases the statement that after a few hours no copper could be detected in the water by the most delicate chemical tests, but have failed to see in any instance an account of the manner of making these tests, or any figures to prove their accuracy.

Owing to the unreliability of these qualitative tests for very small amounts of copper in natural waters, and to the necessity of obtaining quantitative results for purposes of comparison, it has been found that the only satisfactory way is to concentrate a large quantity of the water under examination, separate out the copper in proper condition for electrolysis, and deposit it as metal on a platinum electrode and weigh it.

The amount of water which is concentrated depends upon the amount of copper suspected to be present. Such an amount as will yield a weight of from 5 to 10 milligrams of metallic copper is preferable, as this amount of copper adheres well to the inside of the platinum dish which serves as an electrode, and can be weighed with accuracy on an analytical balance.

If the amount of copper in the water is very small, however, it is necessary to be content with a less weight, in order to avoid concentrating a very large volume of water.

It is the custom in the work of our board to collect three five-gallon carboys of water for each sample. Of this, 50 liters are concentrated for analysis, an equal amount being taken from each carboy and boiled down in three 10- or 14-inch porcelain dishes, with the addition to each dish of a little hydrochloric acid and 5 or 10 c.c. nitric acid. When concentrated as far as possible, the residues are united in one small dish, nitric acid being used to rub off the scum of organic matter which adheres to the sides of the dishes, and after further concentration the whole is treated with strong sulphuric acid and fumed over a lamp for some minutes. By this process, all silica is rendered insoluble, much of the organic coloring matter is destroyed, and the metals present are converted to sulphates. After dilution and filtering, the excess of sulphuric acid is neutralized, and hydrogen sulphide added to the sulphuric acid solution. By this means the rest of the coloring matter is left behind, together with zinc, if present, and practically all of the iron. Lead, if present, will have been previously removed as sulphate. The sulphides are dissolved in nitric acid, converted to sulphates by strong sulphuric acid, and any iron remaining is removed by ammonia. The filtrate from the iron is acidified with sulphuric acid and, as a precaution, is allowed to stand for some time, in which case any lead which remained after the two previous filtrations will deposit as sulphate. The solution is then treated with 10 c.c. of concentrated sulphuric acid and 1 gram of urea and placed in a platinum dish and electrolyzed, the inside of the dish becoming the cathode, while a coil of platinum wire is placed in the solution for the anode. Any zinc which might be present remains in solution; in fact, we have made use of this method for separating quantitatively considerable amounts of zinc from small amounts of copper, or *vice versa.*

When the copper is all deposited, the dish is washed, dried and weighed; then the copper is dissolved off the dish in dilute nitric acid, and the dish dried and weighed again. The difference in weight gives the weight of copper. There is occasionally a very small amount of organic matter, due to the decomposition of the urea or organic matter in the solution adhering to the dish, and insoluble in nitric acid; hence the manner of weighing, instead of taking the weight of the empty dish before the electrolysis.

The solution of the copper in nitric acid may be made ammoniacal, when the characteristic blue color due to copper will appear. It has been found that 0.0001 gm. of copper in a volume of 20 c.c. gives a faint blue color by this test, while 0.0002 gm. copper gives a very distinct color. This represents a sensitiveness of 1 part in 200,000 and 1 part in 100,000, respectively. A set of standards may be made up with known amounts of copper in this condition and the copper obtained by electrolysis can be read on such standards, though 0.0001 gm. copper is the smallest amount that can be detected; and it is impossible to interpolate between successive 10ths of a milligram. The test is of service, however, in verifying the result when the weight of copper obtained is only a few 10ths of a milligram.

Following are a few results obtained by the method with standard solutions, and also with natural waters to which known amounts of copper were added. In every case a considerable quantity of water was treated with the copper solution and then concentrated and carried through in the same manner as an unknown.

TABLE 1.

EXPERIMENTS WITH SOLUTION OF COPPER SULPHATE IN DISTILLED WATER.

Weight of Copper Taken (Gram)	Weight of Copper Found (Gram)
0.0006	0.0005
0.0009	0.0007
0.0021	0.0019
0.0047	0.0050

TABLE 2.

EXPERIMENTS WITH A NATURAL SURFACE WATER TO WHICH KNOWN AMOUNTS OF COPPER SULPHATE WERE ADDED.

Weight of Copper Taken (Gram)	Weight of Copper Found (Gram)	Quantity of Water Concentrated (Liters)
0.0006	0.0008	50
0.0014	0.0017	50
0.0047	0.0048	34
0.0091	0.0085	34
0.0222	0.0202	16
0.0404	0.0360	16

These results show the method to be capable of separating and determining small amounts of copper with considerable accuracy. In studying the figures it appears that the percentage error is quite large, especially in the case of the smaller quantities. It must be borne in mind, however, that the absolute error is very small; in fact, in some instances as small as the analytical balance is capable of detecting. In the case of the larger quantities, an additional error is introduced by dividing the solution before electrolysis, in order to avoid having too heavy a deposit on the dish. All of the results were obtained without previous knowledge by the operator of the amounts of copper present, and the determinations were carried out in all respects as with unknowns.

TABLE 3.

This table shows a series of results obtained from samples of water from a large natural reservoir infested with algæ, to which copper sulphate had been applied. In every case 50 liters of water were taken for analysis; the figures show the weight of copper found in each sample and its approximate dilution.

	Gram		
Before dosing	0.0001	Equivalent to 1 part Cu in	500,000,000
1 day after dosing	0.0025	" " 1 " " "	20,000,000
2 days " "	0.0016	" " 1 " " "	31,250,000
3 " " "	0.0012	" " 1 " " "	41,666,000
7 " " "	0.0006	" " 1 " " "	83,333,000
13 " " "	0.0004	" " 1 " " "	125,000,000
27 " " "	0.0002	" " 1 " " "	250,000,000

These figures show clearly the necessity of operating on considerable quantities of the sample if reliable quantitative results are to be obtained. They show also the fallacy of depending on the ordinary qualitative tests to prove a water free from copper. The most delicate of the various tests would fail to reveal the presence of the metal in the original concentration in any of the foregoing samples, while if the water is subjected to concentration, some provision must be made for the removal of iron and organic coloring matter, or the accuracy of the test is vitiated.

It is believed that the method as devised is the most accurate and satisfactory one at the present time, and, though somewhat tedious, justified by the importance of thoroughly testing this comparatively new process of water purification before passing judgment on its value.

The method may also be used upon sand, the copper being extracted therefrom by means of nitric acid and the subsequent procedure being the same as with a water residue.